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By

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Lower Limits on the Absolute Dissociative Electron Attachment Cross Section from O₂ Condensed on Rare-Gas Films.

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Abstract. We summarize our approach for experimentally obtaining a lower limit on the absolute cross section for production of O⁻ by dissociative electron attachment from O₂ condensed on a Kr film. Comparison of this result with the dissociative attachment cross section for gas phase O₂ reveals a factor of 17 enhancement on the surface. It is semiquantitatively shown that a decreased autoionization rate, arising from the electronic polarization of the neighboring Kr atoms, can account for most of this large enhancement.

1. Introduction

It could be claimed that the simplest system imaginable for studying surface effects is closed-shell molecules condensed on a rare-gas film. This claim is made because of the weak interactions involved. In this paper we summarize previously published work, which to our knowledge accomplishes the first direct comparison of absolute electron dissociation cross-sections in the gas phase and on the surface of a solid. In Sect. 2 we summarize the experimental procedure for obtaining a lower limit on the absolute dissociative electron attachment cross section from O₂ condensed on rare gas films. In Sect. 3 we summarize a semi-quantitative theory for explaining the large enhancement seen in the dissociative cross-section for O₂ on the surface.

2. Experiment

Using low-energy electron transmission spectroscopy (LEETS), two of us (M.D. and L.S.) along with Marsolais [1] have devised a new method to measure surface charges on a thin dielectric film deposited on a metal substrate. In LEETS [2], the electron current arriving at the metal substrate is measured as a function of the potential applied between the substrate and the electron source. When the dielectric film is not charged, the electron current rises sharply at the zero-energy reference (ZER) of the vacuum level as seen in Fig. 1. When electrons are trapped in the
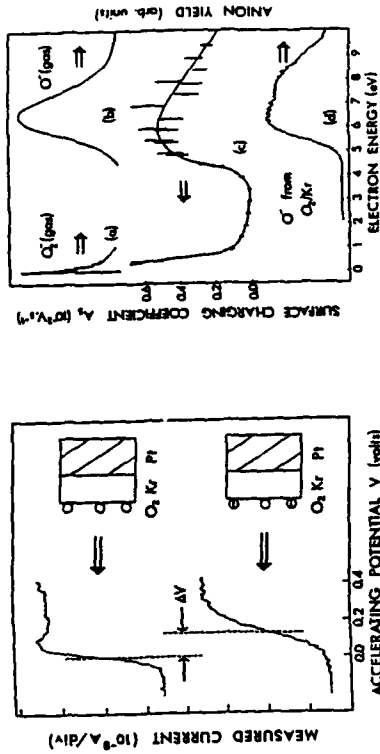
Fig. 1 Current transmitted through a clean Kr layer (top) and that through a Kr layer covered with 0.1-monolayer (ML) of O₂ (bottom) as a function of the incident electron beam voltage, V. (Data from reference 1; Used with permission).

Fig. 2 Anion yields produced by 0-10 eV electron impact on gaseous O₂ (a and b) and on 0.1 ML O₂/Kr (d). The electron energy dependence of the surface charging coefficient A_s for 0.1 ML O₂/Kr is shown in (c). (Data from reference 1; Used with permission).

dielectric or on the surface, this ZER shifts to a higher accelerating voltage because the trapped negative charges retard the incoming electrons. Assuming a charged capacitor model, this ZER shift, ΔV, can be related to an average surface charge density Q by the relation $\Delta V = c^{-1}LQ$, where c and L are the dielectric constant and thickness of the film, respectively [1].

If the dielectric film is covered by molecules with a small surface density, σ_s, and only these molecules can trap electrons, then the average surface-charge density, Q(t), trapped by the molecules after small time, t, can be given, Q(t) = J$\sigma_s\mu$t. Here J is the average electron current density, and μ is the electron trapping cross section. The corresponding ZER shift $\Delta V(t)$ is then $\Delta V(t) = c^{-1}LJ\sigma_s\mu$t. Its time derivative at t=0, denoted by A_s, is,

$$A_s = d\Delta V(t)/dt|_{t=0} = c^{-1}LJ\sigma_s\mu. \tag{1}$$

The proportionality of A_s with L, J, and σ_s has been experimentally verified [1]. No charge accumulation is observed on pure Kr films for thicknesses of 1-20 monolayers (ML) in the electron energy range 4-10 eV [1], indicating that indeed only the O₂ species trap charge.

Figure 2 shows the electron energy dependence of A_s between 0-10 eV [1]. The results are comparable to the energy dependence of the anion yields derived from O₂ in the gas phase. No signal has been reported

between 1.2 and 4.5 eV in the gas-phase. Curve d represents the electron stimulated desorption (ESD) signal from a 0.1 ML O_2/Kr. The similarity of the surface charging coefficient to the gas phase anion yield data shows that the surface charging in the 0-2 eV range is due to vibrational stabilization via the $^2\Pi_g$ O_2^- shape resonance,

$$e^- + O_2(X^3\Sigma_g^-)/Kr \rightarrow O_2^-(^2\Pi_g)/Kr. \qquad (2)$$

The trapping cross-section in the region 4-10 eV is due to dissociative attachment via the intermediate $^2\Pi_u$ state of O_2^- [3],

$$e^- + O_2(X^3\Sigma_g^-)/Kr \rightarrow O_2^-(^2\Pi_u)/Kr \rightarrow O + O^-/Kr. \qquad (3)$$

Since the ESD of O^- from the surface is also known to proceed through this process, the O^- ESD and charging proceed via the same mechanism in this energy region. The small shift in energy between the peaks for the ESD yield and the surface charging coefficient is due to the polarization of the Kr film (see below).

We wish to make a quantitative comparison between the DA cross-sections in the gas phase and on the surface; i.e. comparison of the peak heights in the gas phase from O_2 gas and the charge trapping ratio [4]. To do this quantitatively, estimates must be made of several variables. The film thickness of 20 ML is estimated within 15% accuracy by monitoring the interference structures in LEETS [5]. The O_2 coverage, $\sigma_o = 1/7$ ML, is determined within an accuracy of 15% by verifying that the sticking coefficient of O_2 on Kr and Kr on Kr are the same at 20K. Thus L=20x3-¹/³ and σ_o=(1/7)x4x3⁻¹/²3⁻², and the dielectric constant, ε, of Kr is known

to be $(1.78 \pm 0.01)\times 8.85\times 10^{-12}$ Farad/M [6]. The absolute current density, J $= (1.18 \pm 0.08)\times 10^{-3}$ A/M² [2], is measured by allowing all electrons, including those reflected, to return to the surface. The maximum in A_d around 6 eV is $(1.1\pm 0.1)\times 10^{-3}$ volt/sec. This gives a value from Eq. 1 of $\mu = (2.2 \pm 0.7)\times 10^{-17}$ cm². This can be compared with the cross-section in the gas phase at 6.7 eV of $(1.3 \pm 0.2)\times 10^{-18}$ [7]. Apparently an enhancement of the DA cross-section by a factor of 17 ± 8 occurs on the surface.

3. Theory

The origin of this enhancement is explained using Fig. 3 which schematically shows how a Kr film influences the DA process [4]. The upper curves illustrate the accepted interpretation of the DA process for gaseous O_2, where the intermediate $O_2^-(1\pi_g^3 1\pi_u^2)^2\Pi_u$ state dissociates into the lowest O+O⁻ limit, competing with autoionization into the $A^3\Sigma_u^+$, $C^3\Delta_u$, and $c^1\Sigma_u^-$ states arising from the excited configuration, $1\pi_u^3 1\pi_g^3$ and into the $b^4\Sigma_g^+$, $a_4\Delta_u$, and $X^2\Sigma_g^-$ states arising from the ground configuration, $1\pi_u^4 1\pi_g^3$. The three states arising from the excited configuration, are close to each other and hence are represented by a single potential curve in Fig. 3. According to O'Malley [8], less than 1.3% of the $O_2^-(^2\Pi_u)$ states dissociates into the O+O⁻ limit. About half of the $O_2^-(^2\Pi_u)$ states autoionize into the three states arising from the excited configuration, and the remainder into the three states arising from the ground configuration.

Theoretical expressions for the DA process in O_2 have been derived previously by O'Malley et al. [8]. The potential curve for $O_2^-(^2\Pi_u)$ and its survival probability against autoionization have also been calculated by O'Malley [8]. From this information, the cross-section can be evaluated using the expression [4],

$$\sigma_{dA} = \exp\,(3.4(R_c-R_s)^3 - 376(R_s-R_s)^3 - 41(R_c-R_s)^{2/3}), \qquad (4)$$

where R_s is the turning point (in A°) of the $O_2^-(^2\Pi_u)$ intermediate state at the incident-electron energy E; R_c (=1.44 A°) is the crossing point between the potential curves of the $O_2^-(^2\Pi_u)$ state and the $O_2^+(1\pi_g^3 1\pi_u^2)$ states; and R_e is the equilibrium internuclear distance (1.21 A°) of the O_2 ground state (see Fig. 3). The first two terms in brackets in eq. 4 arise from the Franck-Condon overlap integral between the lowest vibrational state of the O_2 electronic ground state and the vibrational continuum of the repulsive $O_2^-(^2\Pi_u)$ state. The delta-function approximation yields the second term and the first term arises from a first order correction. The third term represents a survival probability of the $O_2^-(^2\Pi_u)$ intermediate state against autoionization. The proportionality constant is nearly independent of the electron energy E, so that it is also nearly independent of R_s. The σ_{dA} reaches a maximum at $R_s = 1.24$ A°, which corresponds to E = 6.8 eV or the energy for the maximum cross-section.

In the presence of the Kr film, the potential curve of the charged $O_2^-(^2\Pi_u)$ state is shifted downward, essentially in parallel, because of an electronic polarization of the neighboring Kr atoms [3]. The dissociation limit O+O⁻ is split into the O/Kr+O⁻ and O+O⁻/Kr limits, separated by the polarization energy. R_e and the three exponential coefficients in eq. 4 are not expected to be severely altered by the downward shift, however, R_t and R_c are altered. To calculate σ_{dA} for O_2/Kr, we need just to estimate the polarization energy.

The surface-polarization energy of the Kr film appears to be about 0.9 eV. The observed shift in the threshold energies (4.4 eV vs 3.5 eV) of
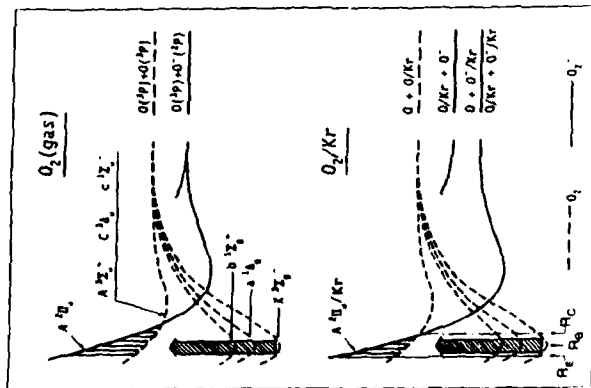

Fig. 3 Schematic potential energy curves (from ref. 4) of O^- (solid curves) and O_2^- (dashed curves) for gaseous O_2 (top) and O_2 physisorbed on a Kr film (bottom). Autoionization of the $O_2^-(A^2\Pi_u)$ and $O_2^-(A^2\Pi_u)$/Kr states are indicated by the downward arrows.

the O⁻ yield from O₂ gas and electron trapping seen in Fig. 2 give 0.9 eV. A theoretical estimate of this energy gave 0.86 eV [9]. The value of R_c has been obtained from an analytical fit of Fig. 3 giving R_c equal to 1.295 A° compared with 1.44 A° in the gas phase [4]. R_g shifts very little, from 1.24 A° in the gas to 1.23 A° on the surface. Insertion of these values into eq. 4 gives an enhancement factor of 21 on the surface. Nearly all of the enhancement comes from the survival factor, the third term in Eq. 4.

It is known that some of the O⁻ produced via DA on the surface escapes or desorbs from the surface (i.e. the source of curve d in Fig. 2). If this fraction, f, is added to the charge trapping yield, we obtain the total DA cross-section on the surface. Therefore, we can equate $17/(1-f)$ to 21, and arrive at an estimate of $f \sim 0.2$. Because of the uncertainties involved, this is a very rough estimate for the probability of desorption from the surface.

We can exclude two other possible explanations for the observed enhancement. The orientation of the O₂ on Kr is fixed, unlike in O₂ gas. The maximum possible enhancement due to orientation dependencies is estimated to be 1.3 [4]. Finally, we have previously discussed an enhancement of O⁻ desorption from Kr due to a coherent scattering phenomena or surface resonance [3]. However, in the current experiment, the incident electron energy is too low for normal-incident electrons to play a role in surface state resonances on Kr. Therefore, the evidence indicates that the polarization effect of the Kr lattice dramatically reduces the autoionization rate, and hence dramatically increases the DA branching ratio on the surface.

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